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(54) DYE-SENSITIZED PHOTOELECTRIC CONVERSION ELEMENT

(57)Abstract:

PROBLEM TO BE SOLVED: To develop an inexpensive photoelectric conversion element using a dye expressed by the general formula (1) and having excellent conversion efficiency and a solar battery. (In the formula Ar¹ and Ar² express an aryl ring or a heterocyclic ring each of which may have a substitute. XYZ express an hydrogen atom or a substitute).

SOLUTION: This solar battery uses the photoelectric conversion element formed of a thin film of an organic dye sensitized semiconductor corpuscle and the thin film is made to carry the dye expressed by the general formula (1).

CLAIMS

[Claim(s)]

[Claim 1] An optoelectric transducer using an oxide semiconductor particle by which sensitization was carried out with coloring matter expressed with a general formula (1).

[Formula 1]

(Ar1 and Ar2 show among a formula the aromatic ring or heterocycle which may have a substituent respectively.) XY and Z express a hydrogen atom or a substituent respectively.

[Claim 2] The optoelectric transducer according to claim 1 which is an aromatic ring in which Ar1 and Ar2 may have a substituent respectively.

[Claim 3] An optoelectric transducer given in claims 1 thru/or 2 wherein Ar1 and Ar2 are the benzene rings thru/or naphthalene rings which may have a substituent respectively.

[Claim 4] An optoelectric transducer given in claims 1 thru/or 3 having at least one or more of a carboxyl group a hydroxyl group a sulfonic group a phosphate group an amide group and a sulfhydryl group in intramolecular.

[Claim 5] An optoelectric transducer using an oxide semiconductor by which united among compounds chosen from a group which consists of organic coloring matter which has one or more coloring matter given in claims 1 thru/or 4 other metal complexes and other structures at least and sensitization was carried out with two or more compounds.

[Claim 6] An optoelectric transducer given in claims 1 thru/or 5 in which an oxide semiconductor particle contains a titanium dioxide as an essential ingredient.

[Claim 7] An optoelectric transducer given in claims 1 thru/or 6 which made an oxide semiconductor particle support coloring matter under existence of an inclusion compound.

[Claim 8] An optoelectric transducer given in any 1 paragraph of claims 1 thru/or 7 produced by making a thin film which consists of oxide semiconductor particles support coloring matter.

[Claim 9] A solar cell using an optoelectric transducer of a statement for any 1 paragraph given in claims 1 thru/or 8.

[Claim 10] An oxide semiconductor particle by which sensitization was carried out with coloring matter expressed with a general formula (1).

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which this invention belongs] This invention relates to the optoelectric transducer and solar cell using the

semiconductor particulate by which sensitization was carried out with organic coloring matter and is a general formula (1) in detail. It is related with the solar cell using the optoelectric transducer and it using the oxide semiconductor particle by which sensitization was carried out with the coloring matter expressed.

[0002]

[Description of the Prior Art] The solar cell which uses sunlight as an energy resource replaced with fossil fuel such as petroleum and coal attracts attention. Now development examinations such as efficient-izing is briskly made about the compound semiconductor solar cell using a crystal the silicon solar cell using amorphous silicon or gallium arsenic etc. etc. However since they have high energy and cost which manufacture takes there is a problem that it is difficult to use it general-purpose. The optoelectric transducer using the semiconductor particulate which carried out sensitization with coloring matter or the solar cell using this is also known and the material and production technology which create this are indicated. (B. O'Regan and M. Graetzel Nature 353 737 (1991) M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos, M. Graetzel, J. Am. Chem. Soc. 115 and 6382 (1993) e. t. c. -- this optoelectric transducer being manufactured using comparatively cheap oxide semiconductor such as titanium oxide and The cheap optoelectric transducer of cost may be obtained compared with the solar cell using conventional silicon etc. and attention is attracted. However in order to obtain an element with high conversion efficiency the complex of the ruthenium series was used as sensitizing dye the cost of coloring matter itself is high and the problem remains also in the supply. Although the trial using organic coloring matter as sensitizing dye has also already been performed it is in the actual condition of not resulting in utilization yet -- conversion efficiency is low.

[0003]

[Problem(s) to be Solved by the Invention] In the optoelectric transducer using an organic-coloring-matter sensitization semiconductor development of the high optoelectric transducer of practicality with high conversion efficiency is called for using cheap organic coloring matter.

[0004]

[Means for Solving the Problem] In order to solve the above-mentioned technical problems as a result of trying hard wholeheartedly this invention persons do sensitization of the semiconductor particulate using coloring matter expressed with the above-mentioned general formula (1) find out that an optoelectric transducer with high conversion efficiency is obtained by creating an optoelectric transducer and came to complete this

invention. Namely this invention [0005] (1) An optoelectric transducer using an oxide semiconductor particle by which sensitization was carried out with coloring matter expressed with a general formula (1) [0006] [Formula 2]

[0007] (Ar1 and Ar2 show among a formula the aromatic ring or heterocycle which may have a substituent respectively.) XY and Z express a hydrogen atom or a substituent respectively.

(2) The optoelectric transducer given in (1) which is an aromatic ring in which Ar1 and Ar2 may have a substituent respectively (3) (1) thru/or the optoelectric transducer given in (2) being the benzene ring thru/or the naphthalene ring in which Ar1 and Ar2 may have a substituent respectively To intramolecular (4) A carboxyl group a hydroxyl group a sulfonic group a phosphate group an amide group (1) thru/or the optoelectric transducer given in (3) having at least one or more of sulfhydryl groups (5) The inside of the compound chosen from the group which consists of organic coloring matter which has one or more coloring matter (1) thru/or given in (4) other metal complexes and other structures at least The optoelectric transducer using the oxide semiconductor by which united and sensitization was carried out with two or more compounds (6) (1) thru/or the optoelectric transducer given in (5) in which an oxide semiconductor particle contains a titanium dioxide as an essential ingredient (7) An optoelectric transducer given in any 1 paragraph of (1) thru/or (7) acquired by making the thin film which consists of an optoelectric transducer (1) which made the oxide semiconductor particle support coloring matter under existence of an inclusion compound thru/or given in (6) and (8) oxide semiconductor particles support coloring matter It is related without the oxide semiconductor particle by which sensitization was carried out with the solar cell using the optoelectric transducer of a statement for any 1 paragraph (9) (1) or given in (8) and the coloring matter expressed with (10) general formulas (1).

[0008]

[Embodiment of the Invention] This invention is explained in detail below. The optoelectric transducer of this invention uses the oxide semiconductor by which is coloring matter expressed with a general formula (1) and sensitization was carried out.

[0009]

[Formula 3]

[0010] As the substituents X and Y in a general formula (1) respectively. Especially the aliphatic hydrocarbon group which may have a substituent although there is no restriction. The amino group which may have a substituent. The aromatic hydrocarbon residue which may have a substituent. The heterocyclic residue. The substitution or the unsubstituted sulfhydryl group which may have a substituent. A hydrogen atom. A halogen atom. An alkoxy group. An alkoxy carbonyl group. Substitution carbonyl group. Such as a carboxyl group. A carbo amide group. And an acyl group. A sulfonic group. A sulfamoyl group. A tosyl group. A cyano group. An isocyano group. A tiocyanato group. An isotiocyanato group. A nitro group. A nitrosyl group. A hydroxyl group. The aliphatic hydrocarbon group which has a phenoxy group. A phosphate group. A phosphoester group. Etc. are mentioned and may have a substituent. The amino group which may have a substituent. The aromatic hydrocarbon residue which may have a substituent. The heterocyclic residue which may have a substituent. A carboxyl group. A hydroxyl group. A sulfonic group. A phosphate group. A sulfhydryl group. Etc. are preferred. And a carboxyl group. A hydroxyl group. A sulfonic group. And a phosphate group are still more preferred. The aliphatic hydrocarbon group which may express the heterocyclic residue which may have the aromatic hydrocarbon residue or the substituent which may have a hydrogen atom. An aliphatic hydrocarbon group which may have a substituent. And a substituent as the substituent Z. And may have a hydrogen atom and a substituent is preferred.

[0011] A straight chain of saturation which may have a substituent as an aliphatic hydrocarbon group. And an unsaturation. Branching. And an annular aliphatic hydrocarbon group are mentioned. A carbon number is a straight chained alkyl group of saturation in which 1 to 36 may have a substituent. Desirable. Still more preferably. And that whose carbon number is 1 to 20 is mentioned. Cycloalkyl of the carbon numbers 3 thru/or 8 etc. are mentioned as an annular thing. As a typical example. A methyl group. An ethyl group. An n-propyl group. An iso-propyl group. An n-butyl group. An iso-butyl group. A ter-butyl group. An octyl group. An octadecyl group. An isopropyl group. A cyclohexyl group. A vinyl group. A propenyl group. Iso [a pentynyl group. A butenyl group. A hexenyl group. A hexa dienyl group. An isopropenyl group. And] -- a xenyl group. And cyclo -- a xenyl group. A cyclopentadienyl group. An ethynyl group. A propynyl group. And a pentynyl group -- it passes. And a KISHINIRU group is mentioned. Iso [a KISHINIRU group. And] and a KISHINIRU group etc. are mentioned. To cyclo.

[0012] Aromatic hydrocarbon residue means a basis excluding one hydrogen atom from aromatic hydrocarbon. For example. A basis excluding one hydrogen atom from aromatic hydrocarbons. Such as

benzene naphthalene anthracene phenanthrene pyrene indene azulene
 fluorene and perylene is mentioned and as these were described above all may
 have a substituent. Usually it is the aromatic hydrocarbon residue which
 has the aromatic rings (condensed ring containing an aromatic ring and
 an aromatic ring) of the carbon numbers 6 thru/or 16. Heterocyclic
 residue means a basis excluding one hydrogen atom from a heterocyclic
 compound. As heterocyclic residue for example pyridine pyrazine pyrimidine
 pyrazole Pyrazolidine thiazolidine oxazolidine Pirana
 chromene Pyrrole benzimidazole imidazoline imidazolidine imidazole A
 pyrazole triazole triazine diazole morpholine Indene indoline thiophene
 franthiazine
 thiazole Indore benzothiazole naphthothiazole oxazole benzoxazole naphthoxazole
 India renin benzo INDO renin pyrazine quinoline quinazoline carbazole etc. are
 mentioned -- each heterocyclic residue -- **** -- it may be
 hydrogenated and these may have a substituent again so that it may
 describe above.

[0013] As a substituent in heterocyclic residue which may have aromatic
 hydrocarbon residue or a substituent which may have an aliphatic
 hydrocarbon group which may have a substituent and a substituent Although
 there is no restriction in particular an alkyl group an aryl group a cyano
 group an isocyano group A tiocyanato group an isotiocyanato group a nitro
 group a nitrosyl group an acyl group A halogen atom hydroxyl a phosphate
 group a phosphoester group substitution or an unsubstituted sulfhydryl
 group Substitution carbonyl group such as substitution or an
 unsubstituted amino group substitution or an unsubstituted amide group an
 alkoxyl group an alkoxyalkyl group an alkoxycarbonyl group a carboxyl
 group a carbo amide group and an acyl group a sulfonic group etc. are
 mentioned. The meaning same as an alkyl group as the above-mentioned is
 expressed and these alkyl groups may be further replaced by the above-
 mentioned substituent (except for an alkyl group). A basis etc. which
 took a hydrogen atom as an aryl group from an aromatic ring mentioned by
 a paragraph of aromatic hydrocarbon residue are mentioned. An aryl group
 may be replaced by the further above-mentioned substituent etc. As an
 acyl group an alkyl carbonyl group of the carbon numbers 1 thru/or 10 an
 aryl carbonyl group etc. are mentioned and an acetyl group a propionyl
 group etc. are preferably mentioned to an alkyl carbonyl group of the
 carbon numbers 1 thru/or 4 and a concrete target. Atom such as
 chlorine bromine and iodine are mentioned as a halogen atom. As a
 phosphoester group a phosphoric acid (carbon numbers 1 thru/or 4) alkyl
 ester group etc. are mentioned. A sulfhydryl group an alkyl sulfhydryl
 group etc. are mentioned as substitution or an unsubstituted sulfhydryl

group. An amino group and mono- **** as substitution or an unsubstituted amino group A dialkylamino groupAs for mono- *****a JI aromatic amino group etc. are mentionedas for mono- *****as for a diethylamino group and mono- *****a dipropylamino group is mentioned***** [mono-]as for a dimethylamino group and mono- *****a diphenylamino group or a benzylamino group is mentioned. It may combine with a core like a durollysine ringand heterocycle may be formed. As substitution or an unsubstituted amide groupan amide groupan alkylamide groupan aromatic amide groupetc. are mentioned. As an alkoxyl groupan alkoxyl group of the carbon numbers 1 thru/or 10etc. are mentionedfor example. As an alkoxyalkyl groupan alkoxy (carbon numbers 1 thru/or 10) alkyl group etc. are mentionedfor example (carbon numbers 1 thru/or 10). As an alkoxycarbonyl groupan alkoxycarbonyl group of the carbon numbers 1 thru/or 10etc. are mentionedfor example. Acidic groupssuch as a carboxyl groupa sulfonic groupand a phosphate grouplithiumA salt like quarternary ammonium saltsuch as metal salt and tetramethylammoniumsuch as sodiumpotassiummagnesiumand calciumtetrabutylammoniumpyridiniumand imidazoliummay be formed. Coloring matter expressed with a general formula (1) may have a counter ion. As a counter ionalthough limitation in particular is not carried outa common anion may be sufficient as it.

As an example F^- Cl^- Br^- I^- ClO_4^- BF_4^- PF_6^- OH^- SO_3^{2-} $CH_3SO_3^-$ - toluenesulfonic acidThey are mentioned by anion etc. which have COO^- - and Br^- I^- ClO_4^- BF_4^- PF_6^- $CH_3SO_3^-$ - toluenesulfonic acidAn anion etc. which have COO^- - are preferred. It may be neutralized by acidic groupssuch as a carboxyl group between not a counter ion but

intramolecularor a molecule. Ar1 and Ar2 in a general formula (1) show an aromatic ring or heterocyclerespectively. As an aromatic ringthe benzene ringa naphthalene ringan anthracene ringa phenanthrene ringThey are mentioned by a pyrene ringa perylene ringan indene ringan azulene ringfluorene ringetc.and as heterocycleA pyridine ringa pyrazine ringa bipyridine ringa piperidine ringa piperazine ringA morpholine ringa phenanthroline ringan indoline ringa thiophene ringa furan ringan oxazole ringa thiazole ringan indole ringa benzothiazole ringa benzo oxazole ringa pyrazine ringa quinoline ringa quinoxaline ringa carbazole ringetc. are mentioned. As Ar1 and Ar2the benzene ring and a naphthalene ring are preferred. Ar1 and Ar2 may be mutually the sameor they may differ.

[0014]Ar1 and Ar2 may have a substituentrespectively. A substituent shown here may be the same as that of a thing quoted by a paragraph of the above-mentioned substituents X and Y. When it may exist and exists [two or more]independently same respectively substituent may be sufficient as two or more substituents of Ar1 and Ar2and they may differ. Coloring matter which has the structure of a general formula (1) to intramolecular Anywayat least one or more carboxyl groupsIt is preferred for adsorption combination with an oxide semiconductor to have substitution carbonyl groupssuch as an alkoxycarbonyl groupa carvone amide groupand an acyl grouphydroxyla sulfonic groupand a phosphate group. Coloring matter expressed with a general formula (1) may form metal and complexessuch as nickelZnand Cu.

[0015]As a typical thing of coloring matter expressed with a general formula (1)kino FUTARON is mentionedfor example. This kino FUTARON an aromatic acid anhydride2-methylquinolineetc. NN-dimethyl sulfoxideIt is obtained by making it condense at 150 ** - about 200 ** using catalystssuch as zinc chloride and p-toluenesulfonic acidamong high boiling point solventssuch as N-methyl pyrrolidonechlorobenzenealt. dichlorobenzenetrichlorobenzeneand sulfolane.

[0016]

[Formula 4]

[0017]Kino FUTARON takes mutually a conjugate structural isomer shown below.

[0018]

[Formula 5]

[0019]The examples of a compound are enumerated below. Both Ar1 and Ar2 express the example of the compound which is the benzene ring to Table 1 as the following general formulas (2). NDM in front shows N and N-dimethylamino groupNDE shows N and N-diethylamino group and NDP shows N and N-diphenylamino grouprespectively.

[0020]

[Formula 6]

[0021]

[Table 1]

[0022]As an example of other coloring matter of thesethe following are mentionedfor example.

[0023]

[Formula 7]

[0024]

[Formula 8]

[0025]Ar1 expresses with the benzene ring the example of the compound whose Ar2 is a naphthalene ring to Table 2 as the following general formulas (3). NDM in front shows N and N-dimethylamino groupNDE shows N and N-diethylamino group and NDP shows N and N-diphenylamino grouprespectively.

[0026]

[Formula 9]

[0027]

[Table 2]

[0028]As an example of other coloring matter of these the following are mentioned for example.

[0029]

[Formula 10]

[0030]With a naphthalene ring Ar₁ expresses the example of the compound whose Ar₂ is the benzene ring to Table 3 as the following general formulas (4). NDM in front shows N and N-dimethylamino group NDE shows N and N-diethylamino group and NDP shows N and N-diphenylamino group respectively.

[0031]

[Formula 11]

[0032]

[Table 3]

[0033]As an example of other coloring matter of these the following are mentioned for example.

[0034]

[Formula 12]

[0035]Both Ar₁ and Ar₂ express the example of the compound which is a naphthalene ring to Table 4 as the following general formulas (5). NDM in front shows N and N-dimethylamino group NDE shows N and N-diethylamino group and NDP shows N and N-diphenylamino group respectively.

[0036]

[Formula 13]

[0037]

[Table 4]

[0038]As an example of other coloring matter of these the following are mentioned for example.

[0039]

[Formula 14]

[0040]The following are mentioned as an example of coloring matter other than these general formula (2) - (5).

[0041]

[Formula 15]

[0042]The dye sensitizing optoelectric transducer of this invention manufactures the thin film of an oxide semiconductor on a substrate using an oxide semiconductor particle and subsequently to this thin film makes coloring matter support. Although that in which the surface is conductivity as a substrate which provides the thin film of an oxide semiconductor by this invention is preferred it is easily available in a commercial scene in such a substrate. On the surface of a polymer material with transparency such as the surface of glass, polyethylene terephthalate or polyether sulphone specifically for example Indium which provided the thin film of metals such as conductive metallic oxides such as tin oxide which doped fluoride and antimony, copper, silver and gold can be used. As the conductivity what is necessary is just usually 1000 ohms or less and especially a thing of 100 ohms or less is preferred. As particles of an oxide semiconductor a metallic oxide is preferred and oxides such as titanium, tin, zinc, tungsten, zirconium, gallium, indium, yttrium, niobium, tantalum and vanadium are mentioned as the example. Oxides such as titanium, tin, zinc, niobium and tungsten are [among these] preferred and titanium oxide is [among these] the most preferred. These oxide semiconductors can also be used mixing although it is single and can also be used. As mean particle diameter the particle diameter of the particles of an oxide semiconductor is usually 1-500 nm and is 5-100 nm preferably. The particles of this oxide semiconductor can also mix and use the thing of big particle diameter and the thing of small particle diameter. A way an oxide-semiconductor thin film forms an oxide semiconductor particle as a thin film on a substrate directly by spray spraying etc. After applying on a substrate the slurry of the method and semiconductor particulate as for which a substrate deposits a semiconductor particulate film electrically as an electrode it can manufacture by drying, hardening or calcinating. The method of using a slurry etc. are preferred on the performance of an oxide semiconductor electrode. In the case of this method a slurry is obtained by distributing the oxide semiconductor particle condensed the 2nd order so that primary [an average of] particle diameter may be set to 1-200 nm into carrier fluid with a conventional method. It is [anything] good if a semiconductor particulate may be distributed as carrier fluid which distributes a slurry. It is preferred for organic solvent such as hydrocarbons such as ketones such as alcohols such as water or ethanol, acetone and an acetylacetone or hexane to be used and to mix and use these and to use water at the point of lessening viscosity change of a slurry. Not less than 300 °C of calcination temperature of the substrate which applied the slurry is usually not less than 400 °C preferably and a maximum is below the melting point (softening temperature) of a substrate in general and a maximum is 900 °C and is usually 600 °C or less preferably. Although there is no limitation in particular in firing time less than 4 hours is preferred in general. The thickness of the thin film on a substrate is usually 5-50 micrometers preferably in 1-200 micrometers. Secondary treatment may be performed to an oxide-semiconductor thin film. Namely for example a thin film can be made to be able to dip in solution such as alkoxide of the same metal as a semiconductor a chloride, a nitrification thing and a sulfide the whole substrate directly and the performance of semiconductor membrane can also be raised desiccation or by re-calcinating. As metal alkoxide titanium ethoxide, titanium isopropoxide, titanium t-butoxide, diisobutyldiacetyl tin etc. are mentioned and the alcohol solution is used. As a chloride titanium tetrachloride, tin tetrachloride, zinc chloride etc. are mentioned and the solution is used.

[0043]Next how to make an oxide-semiconductor thin film support coloring matter is explained. If it is in a solution which

dissolved and obtained coloring matter as a method of making the aforementioned coloring matter supporting with a solvent which may dissolve coloring matter or soluble low coloring matter a method of immersing a substrate with which the above-mentioned oxide-semiconductor thin film was provided is mentioned to dispersion liquid obtained by making distribute coloring matter. Concentration in a solution or dispersion liquid is suitably decided with coloring matter. Semiconductor membrane created on a substrate is dipped into the solution. Dipping time is from ordinary temperature to the boiling point of a solvent in general and dipping time is about 48 hours from 1 hour. As an example of a solvent which can be used for dissolving coloring matter methanol ethanol acetonitrile dimethyl sulfoxide dimethyl formamide etc. are mentioned for example. As for dye density of a solution $1 \times 10^{-6} \text{M} - 1 \text{M}$ are usually good and it is $1 \times 10^{-5} \text{M} - 1 \times 10^{-1} \text{M}$ preferably. Thus an optoelectric transducer of an oxide semiconductor particle thin film which carried out sensitization with coloring matter is obtained. The number of coloring matter to support may be one and it may be mixed in some numbers. When mixing the coloring matter of this invention may be sufficient and other coloring matter and metal complex coloring matter may be mixed. By mixing the coloring matter from which especially an absorption wavelength differs a broad absorption wavelength can be used and a solar cell with high conversion efficiency is obtained. Although there is no restriction in particular as an example of a metal complex to mix J. Am. Chem. Soc. 115a ruthenium complex and phthalocyanine that are shown in 6382 (1993) or JP2000-26487A Porphyrin etc. are preferred and coloring matters such as methine system coloring matters such as phthalocyanine of non-metal porphyrin and cyanine merocyanine oxo Nord and a triphenylmethane series a xanthene series azo the Anthraquinone system is mentioned as organic coloring matter which carries out mixed use. Methine system coloring matters such as a ruthenium complex and merocyanine is mentioned preferably. Although a ratio of coloring matter to mix does not have limitation in particular and it is optimized from each coloring matter it is preferred that beyond a 10% mol grade generally uses it about one coloring matter from mixing of equimolars. It may be the same as that of a case where concentration of the coloring matter sum total in a solution accepts one kind of mixed color matter when adsorbing coloring matter at an oxide semiconductor particle thin film using a mixture solution or a dispersed solution and it supports.

[0044] When supporting coloring matter to a thin film of an oxide semiconductor particle in order to prevent a meeting of coloring matter it is effective under coexistence of an inclusion compound to support coloring matter. Although steroid system compounds such as cholic acid crown ether cyclodextrin calyx allenepolyethylene oxide etc. are mentioned as an inclusion compound here desirable things are cholic acid polyethylene oxide etc. After making coloring matter support the semiconductor electrode surface may be processed with amine compounds such as 4-t-butylpyridine. A way a method of processing dips a substrate with which a semiconductor particulate film which supported coloring matter was provided in an ethanol solution of amine etc. are taken. A solar cell of this invention comprises a photoelectric conversion element electrode a counter electrode a redox electrolyte or a hole transporting material which made the above-mentioned oxide-semiconductor thin film support coloring matter. Redox electrolytes may be a solution in which a redox couple was dissolved into a solvent a gel electrolyte impregnated with a polymer matrix and a solid electrolyte like fused salt. A thing using discotic liquid crystal phases such as conductive polymers such as an amine derivative polyacetylene poly aniline and a polythiophene and polyphenylene as a hole transporting material etc. are mentioned. As a counter electrode to be used it has conductivity and what acts a reduction reaction of a redox electrolyte catalytically is preferred. For example platinum carbon rhodium a ruthenium etc. are vapor-deposited to glass or a high polymer film or what applied a conductive particle can use for it. A halogen oxidation reduction system electrolyte which consists of a halogenated compound and a halogen molecule which use halogen ion as a counter ion as a redox electrolyte used for a solar cell of this invention Although organic acid-ized reduction system electrolytes such as metal redox system electrolytes such as metal complexes such as a ferrocyanic acid salt-ferricyanic acid salt and ferrocene ferricinium ion alkyl thiol alkyl disulfide viologen coloring matter and hydroquinone quinone etc. can be raised A halogen oxidation reduction system electrolyte

is preferred. As a halogen molecule in a halogen oxidation reduction system electrolyte which consists of a halogenated compound-halogen molecule molecular iodine bromine molecules etc. are raised for example and molecular iodine is preferred. As a halogenated compound which uses halogen ion as a counter ion for example although organic quaternary ammonium salt of halogens such as halogenation metal salts such as LiNaIKICsI and CaI or tetra alkyl ammonium iodide imidazolium iodide and pyridinium iodide etc. are raised a salts compound which uses iodine ion as a counter ion is preferred. As a salts compound which uses iodine ion as a counter ion lithium iodide iodination NARIUM iodination trimethyl ammonium salt etc. are raised for example.

[0045] When a redox electrolyte comprises a form of a solution containing an inertness thing is electrochemically used for the solvent. For example acetonitrile propylene carbonate ethylene carbonate 3-methoxy propionitrile methoxy acetonitrile ethylene glycol propylene glycol diethylene glycol triethylene glycol gamma-butyrolactone dimethoxy ethane diethyl carbonate diethylene ether diethyl carbonate dimethyl carbonate 1,2-dimethoxy ethane dimethyl formamide dimethyl sulfoxide 1,3-dioxolane methyl formate 2-methyl tetrahydrofuran 3-methoxy OKISAJI lysine 2-one They are mentioned by sulfolane tetrahydrofuran water etc. and also in these In particular acetonitrile propylene carbonate ethylene carbonate 3-methoxy propionitrile methoxy acetonitrile ethylene glycol and 3-methoxy OKISAJI lysine 2-one etc. are preferred. These may be independent or may be combined two or more sorts and may be used. In the case of a gel electrolyte what uses polyacrylate polymethacrylate resin etc. is mentioned as a matrix. Concentration of a redox electrolyte is usually about 0.1 to 90 % of the weight preferably at 0.01 to 99 % of the weight.

[0046] A solar cell of this invention arranges a counter electrode so that it may be inserted into an electrode of an optoelectric transducer which supported coloring matter to an oxide-semiconductor thin film on a substrate. It is obtained by being filled up with a solution which contained a redox electrolyte between them.

[0047]

[Example] Although this invention is explained still more concretely based on an example below this invention is not limited to these examples. Among an example unless a part in particular specifies % expresses weight % for a weight section again respectively.

[0048] 1.4 copies of synthetic example 1 quinaldines and 1.9 copies of trimellitic anhydride are dissolved in 20 copies of trichlorobenzenes and 0.1 copy of zinc chloride is added here. After stirring at 190 °C for 24 hours the solid which added 40 copies of methanol and deposited was filtered and it swabbed in methanol and dried and 2.8 copies were obtained for the compound 1. Structure was checked by various spectra etc. λ_{max} (DMF): 459 nm [0049] 2.2 copies of pyromellitic anhydrides and 1.7 copies of 3-hydroxy-2-methylquinoline are added to 30 copies of synthetic example 2 sulfolanes After heating at 180 °C and carrying out heating stirring at 200 °C for 1 hour the solid which added 40 copies of methanol and deposited was filtered and it swabbed in methanol and dried and 3.4 copies of compounds 37 were obtained. Structure was checked by various spectra etc. λ_{max} (DMF): 445 nm [0050] 1.7 copies of synthetic example 3 3-hydroxy-2-methylquinoline and 1.9 copies of trimellitic anhydride are dissolved in 20 copies of trichlorobenzenes and 0.1 copy of zinc chloride is added here. After stirring at 190 °C for 24 hours the solid which added 40 copies of methanol and deposited was filtered and it swabbed in methanol and dried and 2.8 copies were obtained for the compound 40. Structure was checked by various spectra etc. λ_{max} (DMF): 416 nm [0051] The coloring matter expressed with an example general formula (1) was dissolved in EtOH so that it might be set to 3×10^{-4} M. A porous substrate (semiconductor thin film electrode which sintered porous titanium oxide on the transparent conductive glass electrode) is immersed from 3 hours at a room temperature into this solution overnight made the coloring matter of general formula (1) structure support it was made to wash and dry with a solvent and the optoelectric transducer of the semiconductor membrane which carried out dye sensitizing was obtained. In Examples 46 and 9 and the comparative example 20. 2M titanium tetrachloride aqueous solution is dropped at the titanium oxide membrane part of

a semiconductor thin film electrode and it rinses after 24-hour settlement at a room temperature. The coloring matter of general formula (1) structure was again supported with 450 degrees in a similar manner using the titanium tetrachloride processing semiconductor thin film electrode obtained by calcinating for 30 minutes. Furthermore, about Example 3 at the time of support of coloring matter, cholic acid was added as an inclusion compound so that it might be set to $3 \times 10^{-2} M$. The previous coloring matter solution was prepared, it supported to semiconductor membrane, and cholic-acid-treatment dye sensitizing semiconductor membrane was obtained. The solution which fixes the electrically conductive glass by which weld slag was carried out with platinum in the surface so that it might insert with this and contains an electrolyte in the opening was poured in. The solution containing an electrolyte -- A and B -- two kinds were prepared. What was dissolved so that the electrolysis solution of A might become 0.1M/0.1M/0.6M/1M at 3-methoxy propionitrile, respectively about an iodine / lithium iodide / 1 and 2-dimethyl-3-n-propyl imidazolium iodide / t-butylpyridine. In the solution of 6 to 4 of ethylene carbonate and acetonitrile, it dissolved and the electrolysis solution of B prepared iodine / tetra-n-propyl ammonium eye ODAIDO so that it might become 0.02M/0.5M. The size of the cell to measure made the execution effect portion 0.25-cm². The light source was made into 100 mW/cm² through AM1.5 filter using 500W xenon lamp. A short-circuit current, release voltage, and conversion efficiency were measured using POTENSIO galvanostat.

[0052]

[Formula 16]

[0053]

[Table 5]

[0054]

[Effect of the Invention] In the dye sensitizing optoelectric transducer of this invention, the solar cell with high conversion efficiency was able to be provided by using the coloring matter of a general formula (1).